SOME STUDIES OF SALT EFFECTS ON SOLUBILITY IN ACETIC ACID

by

Ralph K. Birdwhistell
B. S., The Ohio State University, 1949

Submitted to the Department of Chemistry and the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Advisory Committee:

Redacted Signature

Chairman

Redacted Signature

Redacted Signature

October 1953

The author wishes to express his appreciation to Dr. Ernest Griswold for advice and encouragement throughout the course of this investigation, to the Department of Chemistry for the provision of an assistantship during the first three years, and the Office of Ordnance Research, U. S. Army for the provision of the grant without which this investigation would not have been possible.

TABLE OF CONTENTS

INTRODUCTION

In nonaqueous media wherein the dielectric constant of the solvent is much lower than that of water, the solubility studies which have been reported (1, 2, 3, 4) indicate that the salt effect is very pronounced. It has been found, however, that the simple Debye-Huckel expression, assuming complete dissociation of the salts, does not explain the effects observed, and the Gronwall, LaMer, and Sandved (5, 6) extension of the Debye--Huckel theory of interionic attraction (7) has commonly been used to interpret the data. One result, due to the assumption that all binary electrolytes are completely dissociated, is that the activity coefficients are exceedingly small for the solute even in the most dilute solutions.

Following Bjerrum's introduction of the theory of ion-pairs (8), and the elaboration of the theory by Fuoss and Kraus (9, 10, 11), there have been a series of investigations on solvents of low and intermediate dielectric constant which show that solutions in these solvents are not, in general, amenable to any treatment which assumes complete dissociation of the solute molecules into ions in the solution. The most convincing evidence of this effect, arising from conductivity studies with such solvents as ethylene dichloride, dioxane-water mixtures, and benzene (12), demonstrates that in solutions of uniunivalent salts in these solvents the solute species must be considered to be present

largely as ion-pairs or in more highly associated conglomerates. This conclusion is further substantiated by the cryoscopic studies of Webb (13) and of Eichelberger (14) on acetic acid solutions.

It has been found that the effects of a number of uni-univalent salts upon the solubility of potassium bromide in anhydrous acetic acid, which has a dielectric constant of 6.20 at 30°C. (15), may be explained in terms of an exchange reaction between the ion-pairs of the solvent salt and the solute salt (2, 16). This exchange may be represented by the following equation:

$$K^+Br^- + M^+X^- \rightleftharpoons K^+X^- + M^+Br^- \qquad (I)$$

The extent of exchange taking place in the reaction represented by equation (I) would then depend upon the initial concentration of MX and the value of the equilibrium constant of the reaction. This reaction would then in turn result in displacing the reaction

$$KBr\,(Solid) \rightleftharpoons K^+Br^-\,(Solution) \qquad (II)$$

to the right with a corresponding increase in the amount of solid dissolved.

The present investigation was undertaken for the purpose of obtaining further information on the effects of the solvent salt on the solubility of a solute salt in anhydrous acetic acid. The experimentations involved a study of the effects of potassium, sodium, lithium, and ammonium acetates as solvent salts upon the solubility of ammonium bromide;

the effects of silver acetate, sodium acetate, and lithium nitrate upon the solubility of silver nitrate; and the effects of silver nitrate, sodium acetate, and lithium nitrate upon the solubility of silver acetate in anhydrous acetic acid.

HISTORICAL

In the latter part of the nineteenth century Raoult (17), Raoult and Recoura (18), and Beckmann (19) in some cryoscopic studies in acetic acid noticed that most salts formed almost ideal solutions in this solvent. These investigators found, also, that salts formed nearly ideal solutions in a whole series of solvents, all of which have relatively low dielectric constants. Information of this type appears to have been largely ignored, however, after the publication in 1923 of the Debye-Huckel theory of interionic attraction. This theory had such excellent success in predicting the dependence of the activity coefficient of an electrolytic solute in aqueous solution upon valence type, ionic strength, and temperature that the theory was accepted in its entirety, and in particular the model of complete dissociation for all strong electrolytes in solution was widely accepted.

The theory predicts in an explicit manner a dependence of the activity coefficients of electrolytic solutes upon the dielectric constant of the medium, and in order to test this aspect of the theory a series of investigations were carried out in nonaqueous solvents. One such group of investigations was conducted using salt effects on solubility as a criterion for testing the theory. This group of tests consisted of the work of Robinson in acetone (1); Seward in ethylene dichloride (20); Scholl, Hutchison, and Chandlee

in acetic acid (3); Seward and Hamblet in acetic acid (2); Kraus and Seward in isopropyl alcohol and in methyl acetate (4); Kraus and Seward in acetone (21); Williams and Hansen in ethanol-water mixtures (22) and Williams in methanol (23). Another approach used to test the theory involved cryoscopic studies. Freezing point depression measurements were made by Webb in glacial acetic acid and in liquid ammonia (24); by Eichelberger in anhydrous acetic acid (25); and by Noyes and Baxter in ethanol (26). While agreement with the Debye-Huckel theory or one of its several extensions was found by some workers, those investigators using solvents of sufficiently low dielectric constant found serious discrepancies between theory and experiment.

The Debye-Huckel theory is based upon the assumption that around each ion there exists an "ion atmosphere" created by a Boltzmann distribution of the other ions around it, in which there is a time-average preponderance of ions of opposite sign. This model sets up a resulting charge density which presumably satisfies the Poisson relation. The "ion atmosphere" so created makes a contribution to the electrical potential of the central ion, and this potential is, in turn, reflected in the chemical potential and other related thermodynamic properties of the central ion.

Bjerrum in 1926 (8) modified the Debye-Huckel theory by proposing that whenever an ion approaches to within a certain critical distance of another ion of opposite charge

The two ions become associated into an ion-pair. This ion-pair is essentially a dipole which presumably does not possess an ion atmosphere of its own, nor does it contribute significantly to the ion atmosphere of free ions in the solution. The conditions favoring the formation of such a dipole would be high ionic charge, small ionic radius, and low dielectric constant of the solvent medium, for these conditions are those favoring strong fields. Ion-pairs would, also, be formed more readily in concentrated solutions than in dilute solutions. This modification deals with those conditions under which the Debye-Huckel theory has been least successful.

The treatment proposed by Bjerrmm has been most successful when applied to solutions of low dielectric constant and, in particular, it has given much more reasonable values of the ionic radius parameter appearing in the Debye-Huckel equation. Perhaps the greatest success enjoyed by the Bjerrum theory has been in the explanation of conductance phenomena. The Fuoss and Kraus (9, 10, 27) extension in 1933 of the Bjerrum theory explained the conductance minima frequently observed in non-aqueous solutions in terms of an equilibrium in solution between single-, double-, and triple-ions. This explanation predicts quantitatively how the conductance minimum should shift with varying dielectric constant, and it also accounts for the shape of the Λ-$\sqrt{c}$ curve in the region below which the minimum occurrs. Fuoss and Kraus obtained excellent agreement between theory and experiment in the

study of the conductances of salts in various dioxane-water mixtures as well as in some other solvents. The interpretation provided by Fuoss and Kraus, using the ideas of Bjerrum, provide a much more satisfactory picture of the nature and behavior of solutes in solvents of low dielectric constant than that given by the original Debye-Huckel explanation or by any of the other extensions of that theory.

The use of acetic acid as a solvent for cryoscopic measurements as early as 1884 has been mentioned (17, 18, 19). Much of the work with this solvent, however, dates from about 1928 when Davidson and his co-workers started a series of investigations of its solvent properties. These investigations covered such a wide range of topics as the solubilities, the transference numbers, and the phase diagrams of a large number of salts in anhydrous acetic acid (28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39). Griswold and his co-workers, also, investigated the solubility relationships of salts in some ternary systems in anhydrous acetic acid (32, 37, 40, 41, 42).

With regard to the thermodynamic properties of solutions of salts in anhydrous acetic acid, the data are extremely meager. Webb (24) succeeded in applying an extension of the Debye-Huckel equation to get activity coefficients from his data on the freezing points of lithium bromide, sodium bromide, and sodium acetate solutions in acetic acid. Eichelberger (14) attempted to correlate his freezing point data on ammonium nitrate and sulfuric acid solutions in acetic

acid by an extension of the Debye-Huckel equation, but concluded that the solutes must exist as ion-pairs in solution. Other studies of activity coefficients include those of Hutchison and Chandlee (43) on sulfuric acid solutions using electromotive force measurements; those of Scholl, Hutchison, and Chandlee (3), who determined the solubilities of potassium perchlorate and barium chloride in the presence of added salts; and those of Seward and Hamblet (2), who made a similar investigation using potassium perchlorate and potassium nitrate. Both Eichelberger, and Seward and Hamblet felt that the data were not well represented by any extension of the Debye-Huckel theory, while the other investigators felt that their data were satisfactorily explained by this theory.

Investigations on the conductivities of electrolytes in acetic acid are limited to the work of Kolthoff and Willman (44, 45, 46) who used $HClO_4$, H_2SO_4, HCl, HBr, HNO_3, LiCl, KOAc, NaOAc, and pyridine; of Weidner, Hutchison and Chandlee (46, 47) who employed H_2SO_4, LiCl, KCl, $LiNO_3$, KNO_3, $(CH_3)_4NCl$, $(CH_3)_3(n\text{-}C_4H_9)NBr$, NaCl, NH_4Cl, $NaNO_3$, $CsNO_3$, $(CH_3)_4NBr$, and NaOAc; and of Jones and Griswold (48) who worked with the formates, acetates, and bromides of lithium, sodium, and potassium. Except for Jones and Griswold who explained their results in terms of ion-pair formation, the other authors gave no complete explanation of the data they had obtained. Smith and Elliot (49), whose work depends upon that of Kolthoff and Willman, used indicators to determine

the degree of dissociation of strong acids in anhydrous acetic acid. They came to the conclusion that species present in solution consist essentially of ion-pairs.

In conclusion, one may say that although the data describing the physical state of the solute species in anhydrous acetic acid is comparatively scant, much of the data which has been obtained leads one to believe that electrolytic solutes in this solvent exist largely in associated form.

THEORETICAL

In 1926, shortly after the introduction of the Debye-Huckel interionic attraction theory, Bjerrum published the results of his theoretical investigations upon the effects of ionic association (8). This work involved a calculation of the probability of finding an ion in the neighborhood of a second ion as a function of the radial difference of separation. In deriving this probability distribution Bjerrum assumed, first, that the interionic forces were purely coulombic in nature and, second, that two ions of opposite sign which were closer together than a certain distance would act as a single particle in respect to the resulting colligative properties. Since the ion-pairs would have no net charge, they would have no appreciable effect on the ionic atmosphere of the solution as a whole. The third assumption made was that these ion-pairs existed in equilibrium with single ions, which can be represented by equation (III).

$$M^+X^- \rightleftharpoons M^+ + X^- \qquad \text{(III)}$$

This allows one to write an equilibrium constant expression as follows:

$$K = \frac{[M^+][X^-]}{[M^+X^-]} \qquad \text{(IV)}$$

Since Bjerrum's theory is to be the basis of much of the later discussion, a short outline of it will be given

here. Initially, Bjerrum considered the probability of finding an ion of the i-th kind within a spherical shell of thickness dr at a distance r away from a given central ion to be expressed by

$$H(r)\,dr = \frac{NC_i}{1000}\,4\pi r^2 dr\, e^{-\phi/kT} \qquad (V)$$

C_i is the molarity of the i-th species

N is Avogadro's number

ϕ is the work necessary to separate the i-th ion from the central ion to infinity

Since coulombic forces are assumed to be the only ones operating, Bjerrum writes

$$\phi = \frac{Z_i Z_K \epsilon^2}{Dr} \qquad (VI)$$

D is the dielectric constant

ϵ is the electronic charge

Z_i is the valence of the i-th ion

Z_K is the valence of the central ion

It can be shown that this probability function has a minimum value at

$$r_{min} = \frac{|Z_i Z_K|\epsilon^2}{2DkT} \qquad (VII)$$

Bjerrum next assumes that an ion of opposite charge lying closer to the central ion than r_{min} is to be considered as paired with it. The integration of equation (V) from

a, the distance of the closest approach of the two ions, to r_{min} results in equation (VIII)

$$\alpha = \frac{4\pi N C_i}{1000} \int_a^{r_{min}} r^2 e^{-\frac{Z_i Z_k \epsilon^2}{D r k T}} dr \qquad \text{(VIII)}$$

Bjerrum considers α to be the degree of association.

The evaluation of (VIII) for the case of a single uni-univalent electrolyte yields the result that

$$\alpha = \frac{4\pi N C_i}{1000} \left(\frac{\epsilon^2}{DkT}\right)^3 Q(b) \qquad \text{(IX)}$$

where

$$Q(b) \equiv \int_2^b e^y y^{-4} dy \quad ; \quad y = \frac{\epsilon^2}{D r k T} \quad ; \quad b = \frac{\epsilon^2}{D a k T}$$

The value of the function $Q(b)$ has been tabulated for various values of the argument b ranging from 2 to 80 and the results can be found in the tables of Bjerrum (8) or of Fuoss and Kraus (9).

From the value of α one can readily obtain the equilibrium constant for the ion-pair formation in a solution containing any single uniunivalent electrolyte. This is done as follows:

$$K = \frac{a_{m^+} a_{x^-}}{a_{m^+x^-}} \qquad \text{(X)}$$

Upon substitution equation (X) becomes

$$K = \frac{(1-\alpha)C\,(1-\alpha)C}{\alpha C f_{\mu}} f_{\pm}^{2} = \frac{(1-\alpha)^{2} C f_{\pm}^{2}}{\alpha f_{\mu}} \qquad \text{(XI)}$$

$$K = \frac{\left[1 - \frac{4\pi N C_i}{1000}\left(\frac{\epsilon^2}{DkT}\right)^3 Q(b)\right]^2 C f_{\pm}^{2}}{\frac{4\pi N C_i}{1000} Q(b) f_{\mu}} \qquad \text{(XII)}$$

$f_{\pm}$ is the mean activity of the free ions

f_{μ} is the activity coefficient of the ion-pairs

The activity coefficient of the ion-pairs is assumed to be unity in the dilute solution. Equation (XII) can be, in dilute solution, simplified to

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{\epsilon^2}{DkT}\right)^3 Q(b) \qquad \text{(XIII)}$$

The original assumption that $H(r)dr$ is a probability or that

$$\alpha = \int_{a}^{r_{min}} H(r)\,dr \qquad \text{(XIV)}$$

is not strictly correct since

$$\int_{a}^{\infty} H(r)\,dr \neq 1 \qquad \text{(XV)}$$

These inaccuracies can be shown by the combination of equations (XIII) and (VIII) to give $\alpha = \frac{c}{K}$ and this, in turn, from equation (XII) gives the result that

$$f_{\pm} = \frac{1}{1-\alpha} \qquad \text{(XVI)}$$

which is obviously in error.

These objections to the Bjerrum treatment have been eliminated by the modifications of Fuoss and Kraus (9). Their modification yields equation (XIII) for the ion-pair dissociation constant and approaches equation (IX) only in the limit of infinite dilution. The results of the above treatment when applied to solutions in acetic acid for which D equals 6.20 at 30°C. is that electrolytes when dissolved in this solvent would be expected to exist for the most part as ion-pairs with extremely small concentrations of free ions. This result appears to be substantiated experimentally by the conductance studies which have been made.

It has been proposed by Griswold, Jones, and Birdwhistell (16) that the interpretation of the neutral salt effect in acetic acid ought to take account of the preponderance of ion-pairs in this solvent, and that this may be done in the following way: When two salts, ammonium bromide and a heterionic uniunivalent salt, MX, for example, are placed in anhydrous acetic acid an exchange reaction can be expected to take place. This reaction, represented by

$$(NH_4^+Br^-) + (M^+X^-) \rightleftharpoons (NH_4^+X^-) + (M^+Br^-) \qquad \text{(XVII)}$$

would presumably proceed to equilibrium. The expression for the equilibrium constant is

$$K = \frac{[NH_4^+X^-][M^+Br^-]\,\gamma_{NH_4^+X^-}\,\gamma_{M^+Br^-}}{[NH_4^+Br^-][M^+X^-]\,\gamma_{NH_4^+Br^-}\,\gamma_{M^+X^-}} \qquad \text{(XVIII)}$$

The dissolved ammonium bromide is in equilibrium with solid ammonium bromide and, therefore, we may write

$$a_{NH_4^+Br^-} = [NH_4^+Br^-]\gamma_{NH_4^+Br^-} = S_o\,\gamma_o = \text{Constant} \qquad \text{(XIX)}$$

S_o is the solubility of ammonium bromide in the absence of any other salt

γ_o is the corresponding activity coefficient

Assuming first that the concentration of free ions is negligible when compared to the concentration of ion-pairs, it is easily seen that

$$[NH_4^+X^-] = [M^+Br^-] = \Delta S \qquad \text{(XX)}$$

and that

$$[M^+X^-] = C - \Delta S \qquad \text{(XXI)}$$

where ΔS is the increase in solubility of ammonium bromide

C is the initial molality of the added salt.

The second assumption to be made is that the activity coefficients of the ion-pairs are essentially equal to one

another and constant, or that the activity coefficient ratio is essentially constant.

$$\gamma_{NH_4^+Br^-} = \gamma_{M^+X^-} = \gamma_{NH_4^+X^-} = \gamma_{M^+Br^-} = \gamma_o \qquad \text{(XXII)}$$

Then upon substitution equation (XVIII) becomes

$$K' = \frac{\Delta S^2}{S_o(C - \Delta S)} \qquad \text{(XXIII)}$$

or since S_o is a constant

$$K = K'S_o = \frac{\Delta S^2}{C - \Delta S} \qquad \text{(XXIV)}$$

This equation has been found to apply (16) satisfactorily to the solvent effects of a number of different uni-univalent salts on potassium bromide in anhydrous acetic acid. The justification for assuming that the activity coefficient ratio is constant was explored by Jones (50) and his conclusions based upon the limited data available was that the assumption would not lead to an equilibrium constant differing greatly from that obtained by the use of activities, at least in solutions of relatively low total concentrations.

If it is assumed that in the presence of a salt with a common ion a reaction of the type represented by

$$[NH_4^+Br^-] + [NH_4^+X^-] = [A] \qquad \text{(XXV)}$$

may take place, in which A stands for an association product of the two ion-pairs, then the equilibrium relation corresponding to equation (XXIV) may be written as follows:

$$K_a' = \frac{[A]\,\gamma_A}{[NH_4^+Br^-][NH_4^+X^-]\,\gamma_{NH_4^+Br^-}\,\gamma_{NH_4^+X^-}} \qquad \text{(XXVI)}$$

or

$$K_a = K_a'\,[NH_4^+Br^-]\,\gamma_{NH_4^+Br^-} = \frac{[A]\,\gamma_A}{[NH_4^+X^-]\,\gamma_{NH_4^+X^-}} \qquad \text{(XXVII)}$$

Assuming, as before, the constancy and equality of the activity coefficients and neglecting the small concentration of free ions then

$$[A] = \Delta S$$
$$[NH_4^+X^-] = C - \Delta S \qquad \text{(XXVIII)}$$

and

$$K_a = \frac{\Delta S}{C - \Delta S} \qquad \text{(XXIX)}$$

This relation appears to offer an explanation of the observed small increase in solubility of potassium bromide in the

presence of potassium acetate and potassium formate (16). If one considers that it is possible that association may take place between heterionic ion-pairs as well as between salts bearing a common ion, then it can be postulated that

$$[NH_4^+ Br^-] + [M^+X^-] \rightleftharpoons [A] \qquad \text{(XXX)}$$

and that

$$K_a = \frac{[A]}{[M^+X^-]} \qquad \text{(XXXI)}$$

One may suppose that both association and exchange of ions between pairs are possible in this case. Then taking into consideration both equation (XVII) and equation (XXX) and making the same assumptions as before, the increase in the solubility of ammonium bromide is given by

$$\Delta S = [A] + [NH_4^+X^-] = [A] + [M^+Br^-] \qquad \text{(XXXII)}$$

and the added salt concentration at equilibrium by

$$C - \Delta S = [M^+X^-] \qquad \text{(XXXIII)}$$

and the concentration of the products of the exchange reaction by

$$[NH_4^+X^-] = [M^+Br^-] = \Delta S - K_a(C - \Delta S) \qquad \text{(XXXIV)}$$

Upon the substitution of (XXXII), (XXXIII), and (XXXIV) into equation (XVIII) with some modification and rearranging we have, finally,

$$K = \frac{\Delta S^2}{C - \Delta S} - 2K_2\Delta S + K_a^2(C - \Delta S) \qquad \text{(XXXV)}$$

The object of this investigation will be in part to test the validity of equation (XXXIV), equation (XXIX), and equation (XXXV) in connection with some systems employing solute salts other than potassium bromide.

EXPERIMENTAL

Equipment. For the purification of the acetic acid a pyrex distilling column four feet in height and two inches in diameter packed with pyrex helices was used. This column was equipped with a suitable reflux take-off head.

Pyrex test tubes eight inches in length and approximately one inch in diameter were used as sample containers during the saturation period. These test tubes were drawn-out to approximately one-half inch in diameter near the open end by the use of a blast lamp, were cleaned thouroughly, and were placed in an oven at 135°C. for twelve hours before using. After the sample had been introduced the test tubes were sealed at the neck with an oxygen-gas torch.

The sealed sample tubes were mounted in a stainless steel tumbling device which could accommodate 18 such tubes at a time, and which tumbled them end over end at the rate of 120 times a minute, at the same time keeping them completely submerged in the constant temperature bath. A Cenco bath equipped with a stirrer, two 250-watt knife-edge heaters, and a twelve-inch American Instrument Company mercury thermoregulator, was employed. It was found necessary, particularly during the summer months, to run water which had previously been cooled by the use of a one-third horsepower Temprite water cooler through the cooling coils of the bath. This equipment served to hold the temperature of the bath at 30.00 ± 0.01°C. While the samples were

being equilibrated the temperature was checked frequently with a Beckmann thermometer which had been set against a National Bureau of Standards calibrated thermometer.

After saturation, the samples were filtered through a filtration device described by Cain (51), which was modified by the use of a two-receiver "pig" so that two approximately twenty-gram identical samples could be obtained for analysis. Pressure was applied to the liquid to speed up filtration. The samples were filtered into weighed 30-milliliter glass-stoppered containers, which were then weighed again to give the weight of sample analyzed.

The analysis of the samples was carried out potentiometrically using a Fisher Titrimeter, which was equipped with a silver indicating electrode and an inverted sleeve type of saturated calomel reference electrode. This reference electrode has a built in salt bridge which comes from the factory filled with a solution saturated with ammonium nitrate and potassium chloride. This solution was removed from the bridge part of the electrode and replaced with a solution saturated with sodium nitrate. When the electrode was in use the sodium nitrate solution was replaced every week.

Purification of materials. The anhydrous acetic acid used in this work was prepared from 99.5% commercial c. p. acetic acid. Two liters of this acid was purified at a time by refluxing with a slight excess (in excess of the amount necessary to convert the water present to acetic acid) of acetic anhydride and about 300 milliliters of benzene. The

benzene was thiophene-free and had previously been dried over calcium chloride. The amount of acetic anhydride to be used was calculated from the factor of DeVisser (52). After having been refluxed for 24 hours the mixture was fractionated. If any water remains after the refluxing, it forms an azeotrope with the benzene which boils at 78°C. After the fraction containing the azeotrope and the excess benzene comes off the still, the temperature rises to 116°C., and the fraction boiling between 116°C. and 117°C. is collected. The melting point of this acid was 16.67°C. and it was found to have a specific conductance of 3-4 x 10^{-8} cm. ohm^{-1}. The lowest value of the specific conductance for acetic acid found in the literature is 0.4 x 10^{-8} cm. ohm^{-1} (46) while the accepted melting point is 16.60°C..

The ammonium bromide was prepared from Baker's Analyzed Reagent Grade by extraction with ethanol, followed by recrystalization from this solvent. Approximately 50 grams of the ammonium bromide was placed in the extraction thimble of a Soxhlet extractor and 500 milliliters of absolute ethanol was placed in the distilling flask. This was allowed to reflux until all of the ammonium bromide had dissolved and had recrystallized in the distilling flask. After the above process had been repeated twice more with replacement of the ethanol each time, the ammonium bromide was placed in a vacuum oven at 70°C. for two hours, taken out, ground in a mortar, and replaced in the oven for 24 hours. The product of this purification was assayed at 99.97% on the basis

of the bromide found. The analysis was carried out by placing a weighed amount of the salt in a previously calibrated volumetric flask, and titrating aliquot parts of the solution with standard silver nitrate by the use of the titrimeter.

The silver nitrate was purified by the method of Richards and Wells (53). It was assayed for silver by gravimetric means, using the method of Kolthoff and Sandell (54), and was found to correspond to 99.96% silver nitrate.

Sodium acetate and potassium acetate were purified by subjecting the reagent grade materials to recrystallization three successive times from distilled water at a temperature above the melting point of the hydrate. The recrystallized salts were then dried at 110°C. for two days. To analyze these salts they were converted to the sulfate (55, 56). The assay was 99.93% and 99.89% for sodium and potassium acetate respectively. This material was qualitatively checked for the presence of other metals as impurities by spectrographic means and no impurities were found.

The lithium acetate was prepared and purified by E. Griswold, while the lithium nitrate used was purified from Baker's Analyzed Reagent Grade by recyrstallizing three times from conductivity water. The recrystallized salt was then dried for four days at 80°C. in a vacuum oven. These materials were checked for the presence of impurities by spectrographic means. The water content was checked by dissolving the salt in methanol and titrating with Karl Fischer reagent,

with the result that no water was found within the limits of accuracy of the titration. The silver acetate was purified by shaking for three days in anhydrous acetic acid, then repeating the process with fresh acetic acid. A third similar treatment was used to obtain a master solution of silver acetate for experiments in which it was to serve as a solvent salt. The excess solid silver acetate remaining from this last step, after being dried in a vacuum oven for two days at 40°C., was assayed (54) as 99.86% pure on the basis of the silver found. This solid was used as the solute salt in later solubility studies.

Since the ammonium acetate used was never needed in the dry solid state, it was deemed advisable to make a stock solution containing ammonium acetate in acetic acid. This was done by passing ammonia, which had been dried over sodium, into a previously weighed quantity of pure acetic acid and then weighing the resulting solution. From the gain in weight, the molality of the ammonium acetate solution could be calculated. All salts, solutions, and other materials were stored in a dry box or desiccator over phosphorus pentoxide.

Preparation of solubility samples. The solvent salt stock solutions were made up in one liter quantities. A weighing bottle containing approximately the desired amount of solvent salt was weighed on an analytical balance, the contents transferred to a tared volumetrid flask, and the bottle reweighed. The amount of acetic acid subsequently

used to prepare the solution was determined by weighing the flask and its contents on a large balance sensitive to 0.5 mg. From these data the molality of the stock solution could be calculated. To prepare more dilute solutions approximately 60 grams of the stock solution was introduced into a weight buret from which weighed portions could be delivered into volumetric flasks and diluted with known weights of acetic acid. The concentrations of the master salt solutions were approximately 0.1, 0.01, 0.001 molal. All transfers of solvents and salts were performed in a dry box which was kept anhydrous with phosphorus pentoxide and with a stream of oil pump nitrogen.

The method described above was used whenever the salt was sufficiently soluble in acetic acid. If this condition was not met, a saturated solution of the salt was made up by agitating an excess of the salt in acetic acid on a mechanical shaker for from one to three days and then used as the master solution. This method was used in the preparation of master solutions of silver acetate and silver nitrate for use as solvent salts. The concentration of the solution was determined by titrating the solution by the same method that was used for assaying the samples.

The preparation of the sample proper was done in the following manner. Master salt solutions and pure acetic acid were placed in weight "burets" which were simply polyethylene squeeze bottles; then varying amounts of the salt solution and of the pure solvent were introduced on to an

excess of the solute salt in the test tube ampules. The amount of solvent and solution used was determined by weighing the burets both before and after each sample was prepared. After precautions had been taken to prevent entrance of any moisture, the ampules were sealed with the aid of an oxygen-gas torch.

The samples so prepared were placed in the bath at 30.00 ± 0.01°C. and allowed to equilibrate for from seven to thirty days (usually about 14 days).

Analysis. After equilibrating, the samples were taken from the bath, the tip of the test tube broken, and the solution filtered into tared cells. The cells and solution were then weighed. The solution was transferred quantitatively to a beaker, and analyzed as described below. The samples in which ammonium bromide had been used as the saturating salt were treated with five drops of 10% sulfuric acid to promote coagulation of the silver salt, and titrated potentiometrically, using the titrimeter, with approximately 0.01 N standard silver nitrate.

In the systems employing silver nitrate or silver acetate as saturating salt, the silver content was determined similarly by potentiometric titration using 0.005 N potassium iodide solution which had been previously standardized against standard silver nitrate solution. All standardizations were carried out using the same method that is used when assaying the samples, and approximately 20 milliliters of acetic acid was added so that all conditions would be similar.

Portions of the solid phase from representative samples were analyzed to check for the formation of solvates, mixed salts, or the presence of the solvent salt in the solid phase. For the ammonium bromide system a series of samples were made up, equilibrated, filtered, and the moist solid phase was analyzed for bromide by the method previously described. The solid phases from the systems involving silver salts, were filtered, dried in a vacuum oven, and analyzed for silver. For the systems involving both silver nitrate and silver acetate, samples of the solid phases obtained from the mixtures having the highest concentration of solvent salt were analyzed for carbon and hydrogen,* as well as for silver.

Qualitative tests for sodium were run on the solids obtained from some of the sodium acetate-silver nitrate mixtures. This was done by washing the solid first with acetic acid, then shaking it up with water. The silver in the resulting aqueous solution was precipitated with hydrochloric acid, the filtrate evaporated to dryness, the residue taken up in 1 ml. of water, and zinc uranyl acetate solution added. Quantitative determinations of sodium were carried out on two solutions as follows: The sample was filtered and weighed as described above, the silver was precipitated as the chloride, the solution filtered, the filtrate evaporated to

---

* Microanalytical determinations for carbon and hydrogen were run by G. Weiler, Microanalytical Laboratory, 164 Banbury Road, Oxford England

dryness, taken up with 1 ml. of water, and the sodium precipitated as sodium zinc uranyl acetate, and the rest of the gravimetric procedure was standard (57).

RESULTS AND DISCUSSION

The data obtained from the study of the effects of sodium acetate as the solvent salt on the solubility of ammonium bromide in anhydrous acetic acid are presented in Table I and in Figure I; the effects of potassium acetate as the solvent salt are presented in Table II and in Figure II; for lithium acetate as the solvent salt, the results are given in Table III and in Figure III; and with ammonium acetate as the solvent salt, the results are presented in Table IV and in Figure IV.

The data recorded during the investigations upon silver nitrate as the solute salt are presented as follows: silver acetate as the solvent salt, Table V and Figure V; lithium nitrate as the solvent salt, Table VI and Figure VI; and sodium acetate as the solvent salt, Table VII and Figures VII and VIII.

The data observed while using silver acetate as the solute salt are presented as follows: silver nitrate as the solvent salt in Table VIII and Figure IX; sodium acetate as the solvent salt in Table IX and in Figure XI; and lithium nitrate as the solvent salt in Table X and Figure XII. Since the data in Tables V and VIII deal with different aspects of the same system, that of silver acetate-silver nitrate-acetic acid, it was deemed advisable to represent the combined results graphically in one diagram, Figure X, in order to bring out more clearly the relationships involved.

The system ammonium bromide- alkali metal or ammonium acetate-acetic acid. The solubility of ammonium bromide in acetic acid alone at 30°C. was found to be 0.007692 molal. The results given in Tables I - III and plotted in the corresponding figures demonstrate the characteristic effect of heterionic solvent salts on the solubility of a solute salt in this solvent. All three of the salts, sodium acetate, potassium acetate, and lithium acetate produce a marked increase in the solubility of ammonium bromide. Moreover, the form of the solubility curve obtained in each case is similar, at least superficially, to those which have been described for other systems by previous investigators (2, 3). A comparison of the effectiveness of the three salts shows that at a given concentration sodium acetate produces the greatest increase in solubility, lithium acetate the least. Thus in a solution containing solvent salt at 0.1 molal concentration, the solubility of ammonium bromide is found to be 0.027 molal in sodium acetate solution, 0.024 in potassium acetate solution, and 0.021 in lithium acetate solution. The relative effectiveness of sodium and lithium acetate corresponds to that reported with potassium bromide (16) as the saturating salt.

A closer examination of the data, however, brings to light some significant differences between the results of the present investigations and those previously reported for systems involving potassium bromide. It was pointed out that with potassium bromide as the saturating salt, one

Table I

System Ammonium Bromide-Sodium Acetate-Acetic Acid at 30°C.

Concentration of* Sodium Acetate C.	Solubility of* Ammonium Bromide S.	K (equation XXIV)
0.0000000	0.007692	--------
.0007645	.008095	0.000450
.001025	.008514	.00333
.001225	.008698	.00460
.001320	.008812	.00630
.001470	.009004	.0111
.003711	.01119	.0578
.005057	.01209	.0295
.005745	.01249	.0242
.005835	.01259	.0257
.007223	.01324	.0184
.01039	.01475	.0150
.01311	.01569	.0125
.01963	.01730	.00920
.02382	.01807	.00802
.02739	.01888	.00773
.03039	.01940	.00736
.03131	.01942	.00701
.04122	.02143	.00687
.04165	.02155	.00691
.04400	.02160	.00642
.04425	.02164	.00642
.04657	.02193	.00626
.04673	.02215	.00648
.05360	.02285	.00597
.05416	.02299	.00602
.05472	.02307	.00601
.05997	.02363	.00577
.06586	.02430	.00561
.07334	.02515	.00544
.09160	.02691	.00511
.1051	.02827	.00501
.1522	.03285	.00498

Solid phase: Ammonium bromide throughout

---

* Concentrations reported throughout all tables in this thesis are expressed in moles per 1000 g. of acetic acid.

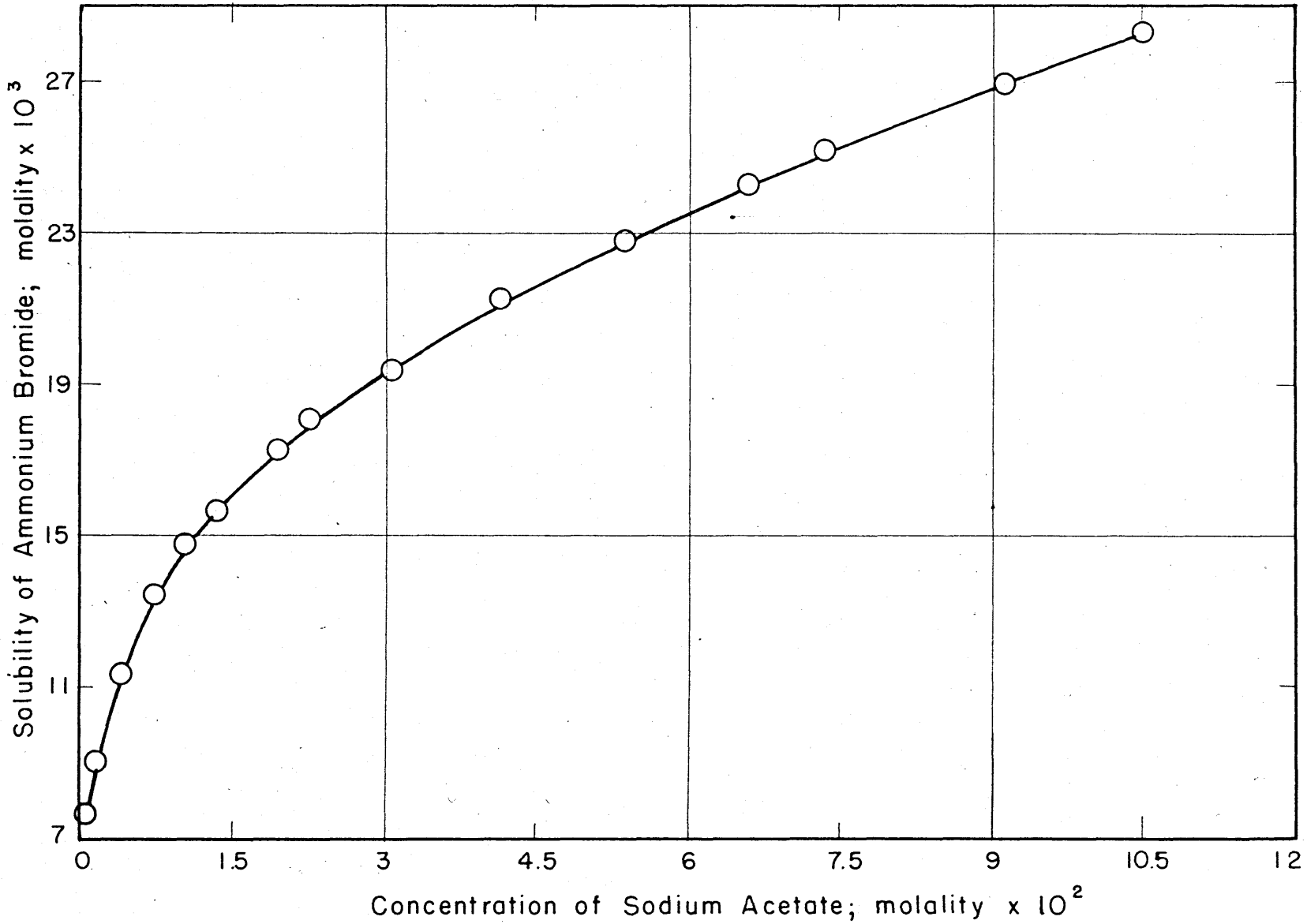

Figure I Solubility of Ammonium Bromide in the presence of Sodium Acetate

Table II

System Ammonium Bromide-Potassium Acetate-Acetic Acid

Concentration of Potassium Acetate C.	Solubility of Ammonium Bromide S.	K (equation XXIV)
0.00000000	0.007692	--------
.0005186	.008094	--------
.001074	.008690	--------
.001211	.008888	--------
.001521	.009250	--------
.001563	.009250	--------
.002507	.009922	0.0179
.004004	.01118	.0236
.006570	.01291	.0202
.007055	.01346	.0258
.007240	.01321	.0177
.008708	.01390	.0155
.01037	.01481	.0157
.01194	.01545	.0144
.01419	.01710	.0185
.02770	.02044	.0109
.03378	.02145	.00945
.05126	.02259	.00611
.06470	.02320	.00489
.08986	.02416	.00370
.1077	.02470	.00319

Solid phase: Ammonium Bromide throughout

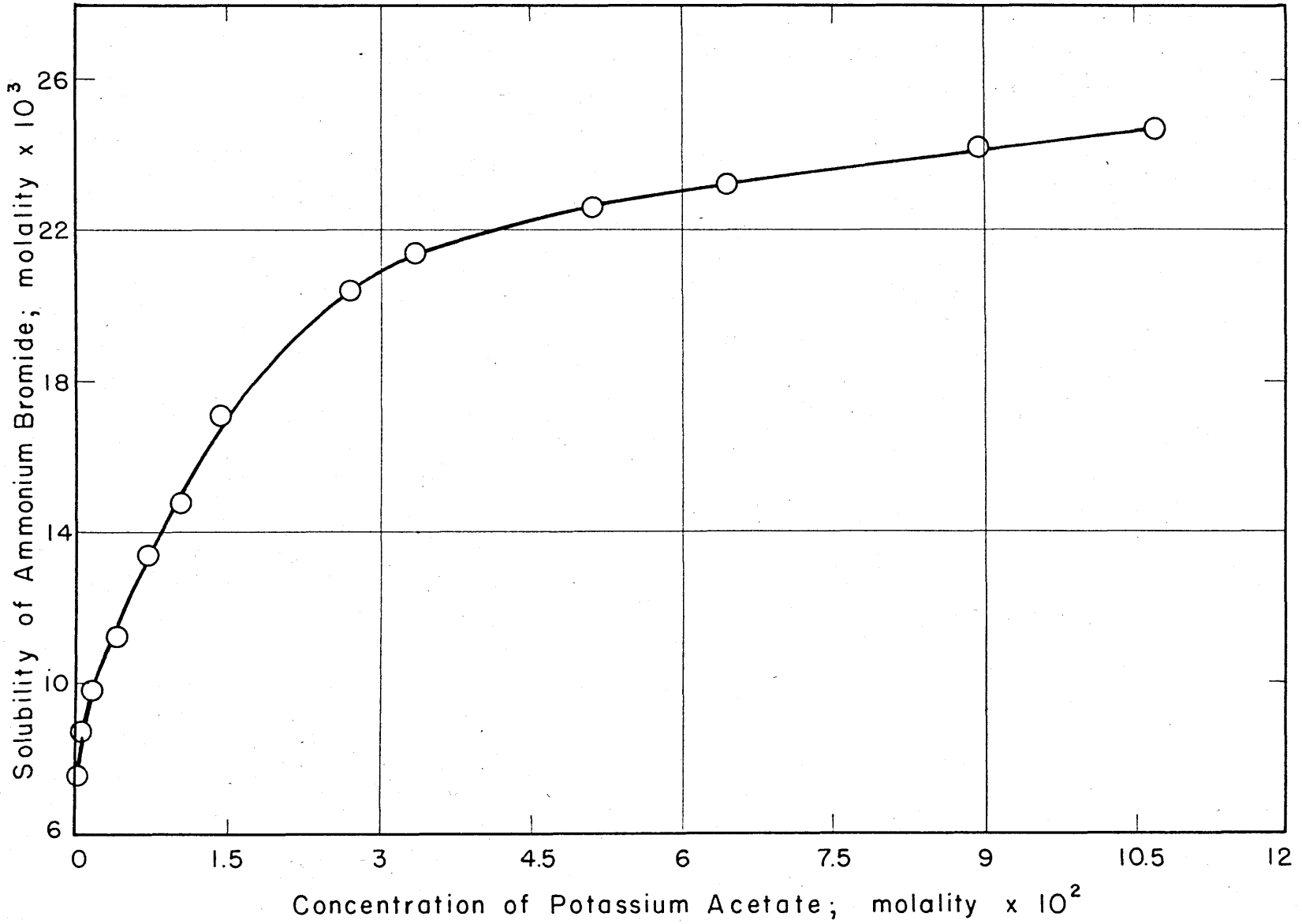

Figure II Solubility of Ammonium Bromide in the presence of Potassium Acetate

Table III

System Ammonium Bromide-Lithium Acetate-Acetic Acid at 30°C.

Concentration of Lithium Acetate C.	Solubility of Ammonium Bromide S.	K (equation XXIV)
0.000000	0.007692	-------
.005403	.009847	0.00228
.004749	.01003	.00198
.009292	.01113	.00202
.01680	.01261	.00203
.02513	.01327	.00159
.02527	.01362	.00182
.03058	.01470	.00208
.03575	.01500	.00189
.03792	.01526	.00189
.04536	.01611	.00192
.05253	.01710	.00194
.06215	.01800	.00205
.06888	.01870	.00209
.07429	.01921	.00212
.07553	.01928	.00210
.09500	.02065	.00205
.1197	.02242	.00207
	Average	.00200
	Ave. Dev. ..	.00011

Solid phase: Ammonium Bromide throughout

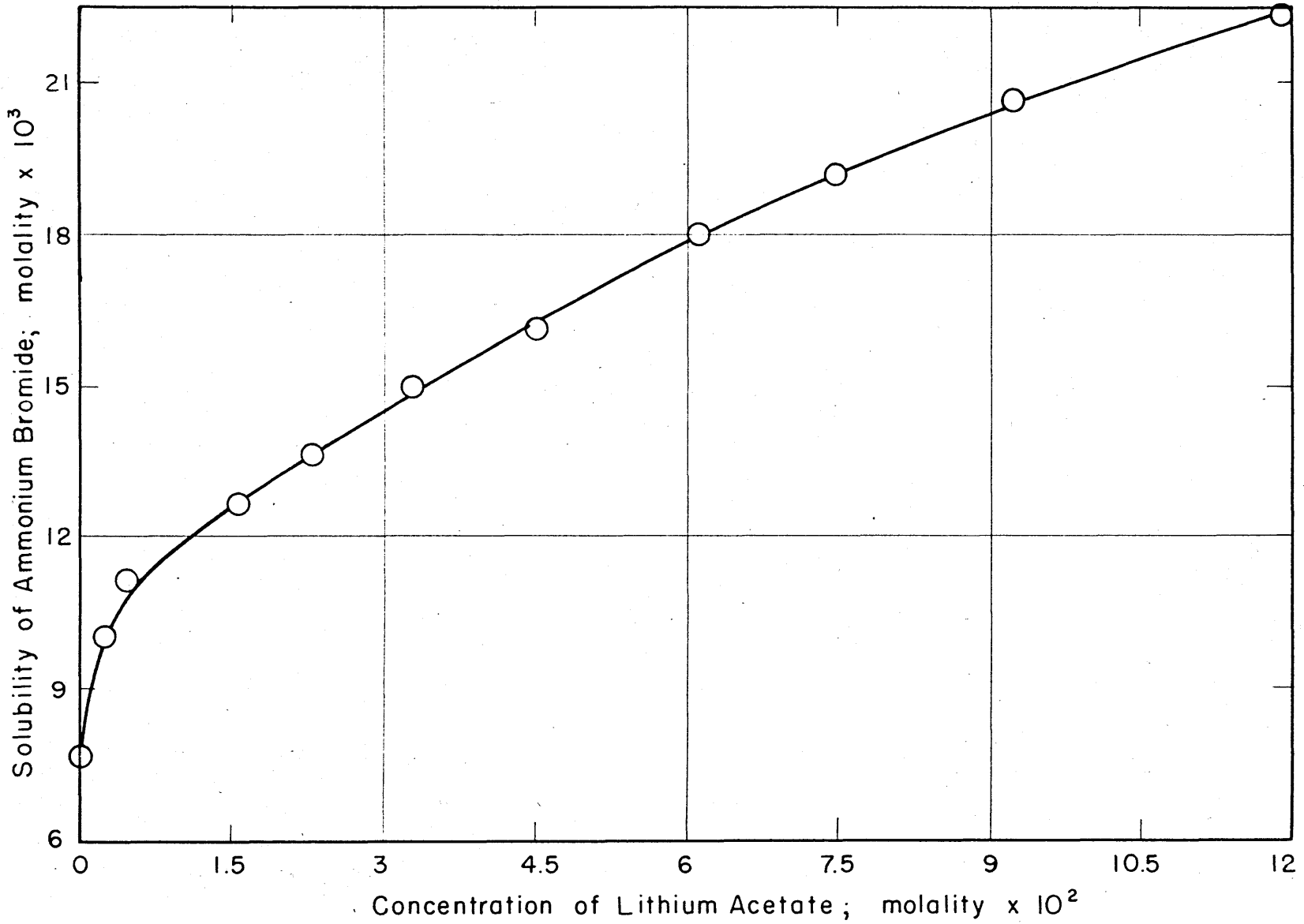

Figure III Solubility of Ammonium Bromide in the presence of Lithium Acetate

Table IV

System Ammonium Bromide- Ammonium Acetate-Acetic Acid at 30°C.

Concentration of Ammonium Acetate C.	Solubility of Ammonium Bromide S.	K_a (equation XXIX)
0.00000	0.007692	-------
.006443	.007742	0.00782
.02270	.007900	.00925
.04831	.008590	.0189
.1009	.01000	.0234
.2064	.01285	.0256
.2187	.01315	.0256

Solid phase: Ammonium Bromide throughout

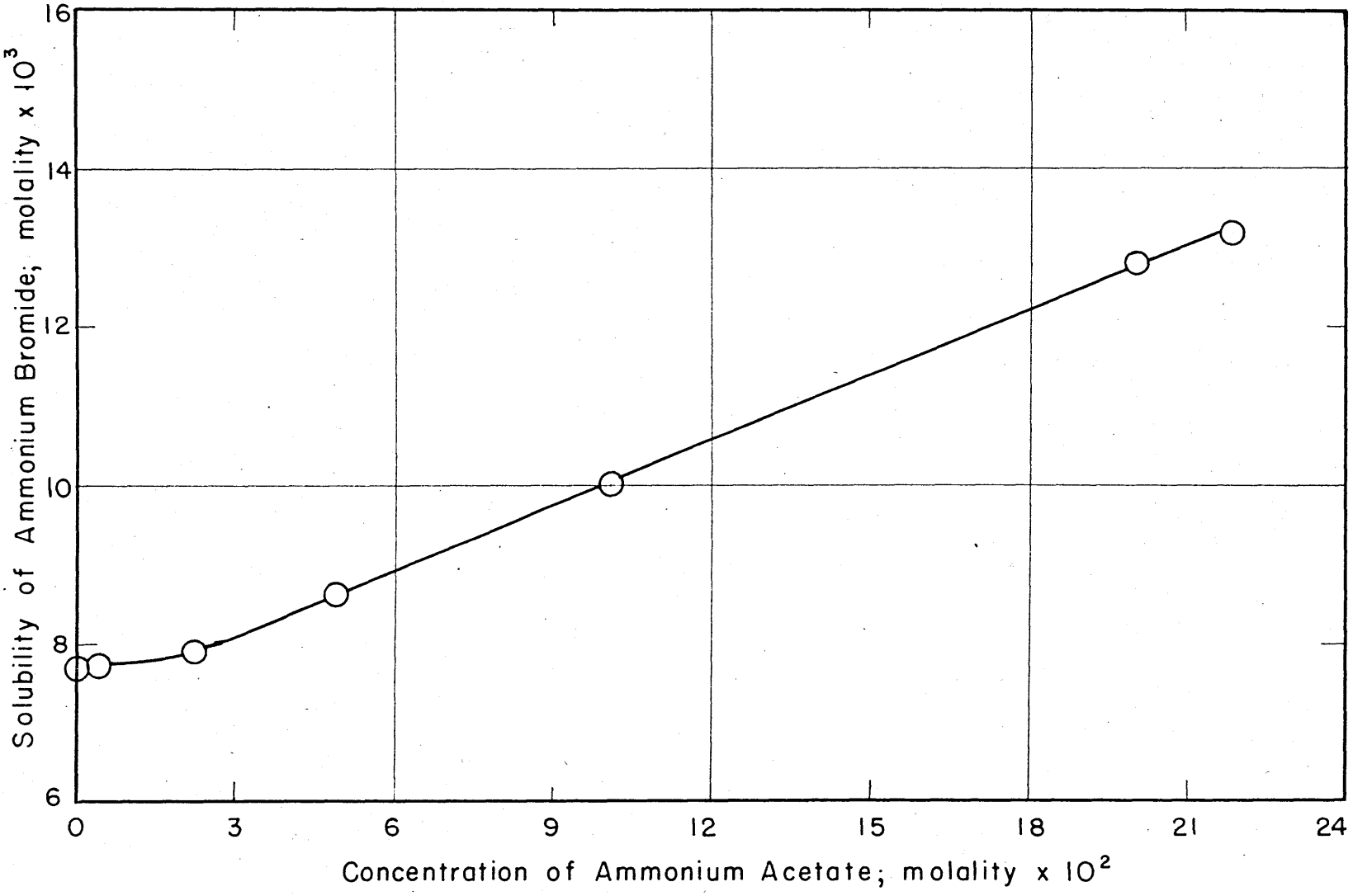

Figure IV Solubility of Ammonium Bromide in the presence of Ammonium Acetate

may postulate the simple exchange reaction

$$K^+Br^- + M^+X^- \rightleftharpoons K^+X^- + M^+Br^- \qquad \text{(XXXVI)}$$

which then leads to an equilibrium constant expression in terms of C and ΔS, equation XXIV. When K is calculated in this way, using the data for sodium acetate as solvent salt and ammonium bromide as solute salt, the values are found to start low, to rise sharply to a maximum, and then to descend, as shown in the third column of Table I. The variation is so pronounced as to leave no semblance of constancy in "K". Potassium acetate displays a similar behavior, as is indicated by the values of "K" in the third column of Table II. In this case, however, the variation in K is not nearly so marked. Finally, lithium acetate shows what might be called a normal effect. In this case K is essentially constant at 0.00200, with no trend indicated.

The unusual behavior of sodium acetate and potassium acetate cannot, of course, be interpreted in terms of a simple ion-pair exchange reaction, but points to the involvement of a more complicated process. The relatively high values of ΔS in the region of low concentration of added salt suggest the formation of more or less complex aggregates involving, perhaps, several ammonium bromide ion-pairs associated with each sodium or potassium acetate ion-pair. This would be expected to result in a pronounced solubilization of the ammonium bromide even at low concentrations of added salt. With an increase in concentration of added salt

beyond a certain range, it is conceivable that the predominant process might be a breaking down of these aggregates into simpler groups involving a higher ratio of solvent salt to ammonium bromide. The formation of simple ion-pairs of the type $NH_4^+OAc^-$ and M^+Br^- might become important in the higher range of solvent salt concentration. The formation of complex aggregates, if this is what does occur, would appear to be a property more or less peculiar to the ammonium ion, but also influenced by the nature of the metal ion of the added salt. Possibly lithium acetate does not produce the effect because of a high degree of solvation and consequently a large effective radius of the lithium ion, resulting in a weaker force field around this ion-pair dipole. It is conceivable that hydrogen-bonding involving the ammonium ion and the negative oxygens of the acetate ion may play an important part in accounting for the unusual behavior of ammonium bromide.

The effect of a salt having an ion in common with the solute salt is shown in Table IV and Figure IV, where the solubility of ammonium bromide in the presence of ammonium acetate in concentrations up to about 0.22 molal is reported. As the curve indicates, there is no evidence of a decrease in solubility at any concentration of added salt. On the contrary the solubility of ammonium bromide actually increases with increasing concentration of ammonium acetate. Above about 0.025 molal concentration of the latter salt, the effect becomes especially pronounced, and it is seen that in

this region ΔS varies linearly with C, the concentration of ammonium acetate. This linear relation between ΔS and C is precisely what would be predicted if association between the two salts in solution occurred in the manner represented by equation (XXIX). From the slope of the line a value of K_a equal to 0.028 is calculated. Below about 0.025 molal with respect to ammonium acetate the slope of the curve decreases, which may indicate the formation of another type of aggregate in this region.

On the whole the solubility behavior of ammonium bromide described in this thesis would appear to give evidence that the formation of aggregates of associated ion-pairs (presumably) is of very considerable importance in the interpretation of salt effects here. Ion-pair exchange between heteroionic salts occur also, but this phenomenon alone does not offer an adequate explanation of the solvent effects observed, except, perhaps for the system involving lithium acetate as the solvent salt.

The systems silver nitrate-uniunivalent solvent salt-acetic acid. It was pointed out in the proceeding section that ammonium acetate, even though it has an ion in common with ammonium bromide, nevertheless produces no decrease in solubility of the latter. Similar absence of the familiar "common-ion" effect has been noted in previous investigations in this solvent. One marked exception to this type of behavior has been reported by Davidson and Geer (34), who observed that the solubility of silver nitrate in the pre-

sence of lithium nitrate at first goes through a pronounced minimum and then increases as the concentration of solvent salt is increased. This suggested that there might be something unusual about the behavior of silver nitrate and perhaps that of other silver salts in acetic acid which it would be of interest to investigate.

Although silver acetate itself has a rather low solubility, as will be shown in the next section, its solubility is sufficient to permit its use as a solvent salt in low concentrations; Table V and Figure V give values of the solubility of silver nitrate in solutions of silver acetate of concentrations ranging up to about 0.004 molal. There is a distinct decrease in solubility throughout this region, as the curve shows. Because of the low solubility of silver acetate itself and the probable "common-ion" effect of silver nitrate upon it, the solid phase in equilibrium with solution containing the highest concentration of silver acetate was analyzed for silver and for carbon and hydrogen. The silver analysis corresponded to 99.97% silver nitrate, but because the molecular weights of silver nitrate and silver acetate are not widely different, it was thought advisable to have the additional analyses made. Microanalytical determinations of carbon and hydrogen in the solid yielded only trace amounts, indicating that the solid phase was indeed silver nitrate.

For completeness the effect of lithium nitrate on silver nitrate solubility was reinvestigated, and the results

Table V

System Silver Acetate- Silver Nitrate-Acetic Acid

Concentration of Silver Acetate C.	Solubility of Silver Nitrate S.
0.0000000	0.006166
.0005529	.005951
.001073	.005832
.001110	.005822
.002661	.005346
.002757	.005359
.003871	.004974

Solid phase: Silver nitrate throughout

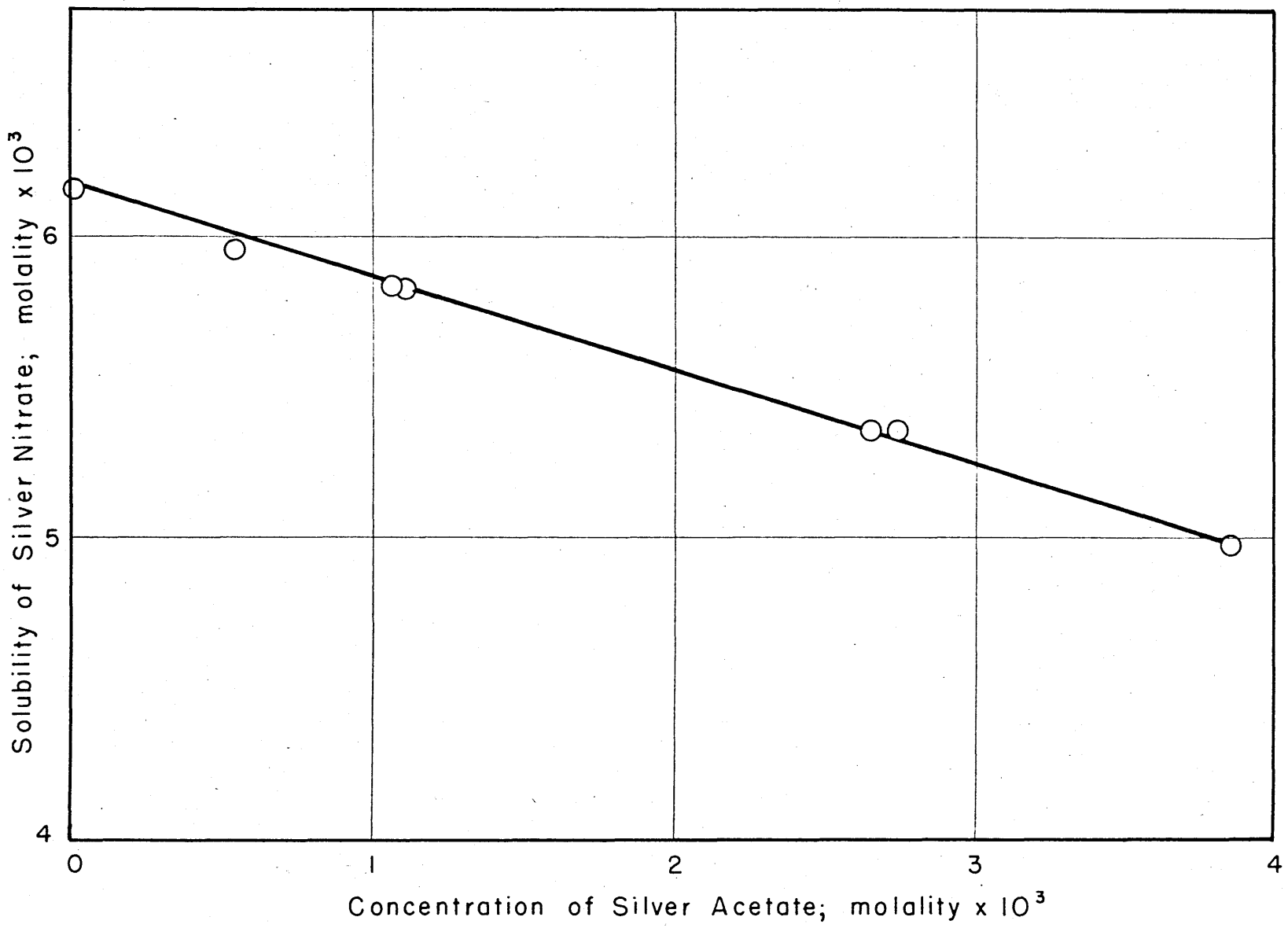

Figure V Solubility of Silver Nitrate in the presence of Silver Acetate

Table VI

System Lithium Nitrate-Silver Nitrate-Acetic Acid at 30°C.

Concentration of Lithium Nitrate C.	Solubility of Silver Nitrate S.
0.000000	0.006166
.005947	.005524
.01031	.005451
.01602	.005248
.01699	.005220
.02290	.005103
.03288	.005177
.03417	.005136
.04902	.005329
.05914	.005593
.08945	.006976

Solid phase: Silver nitrate throughout

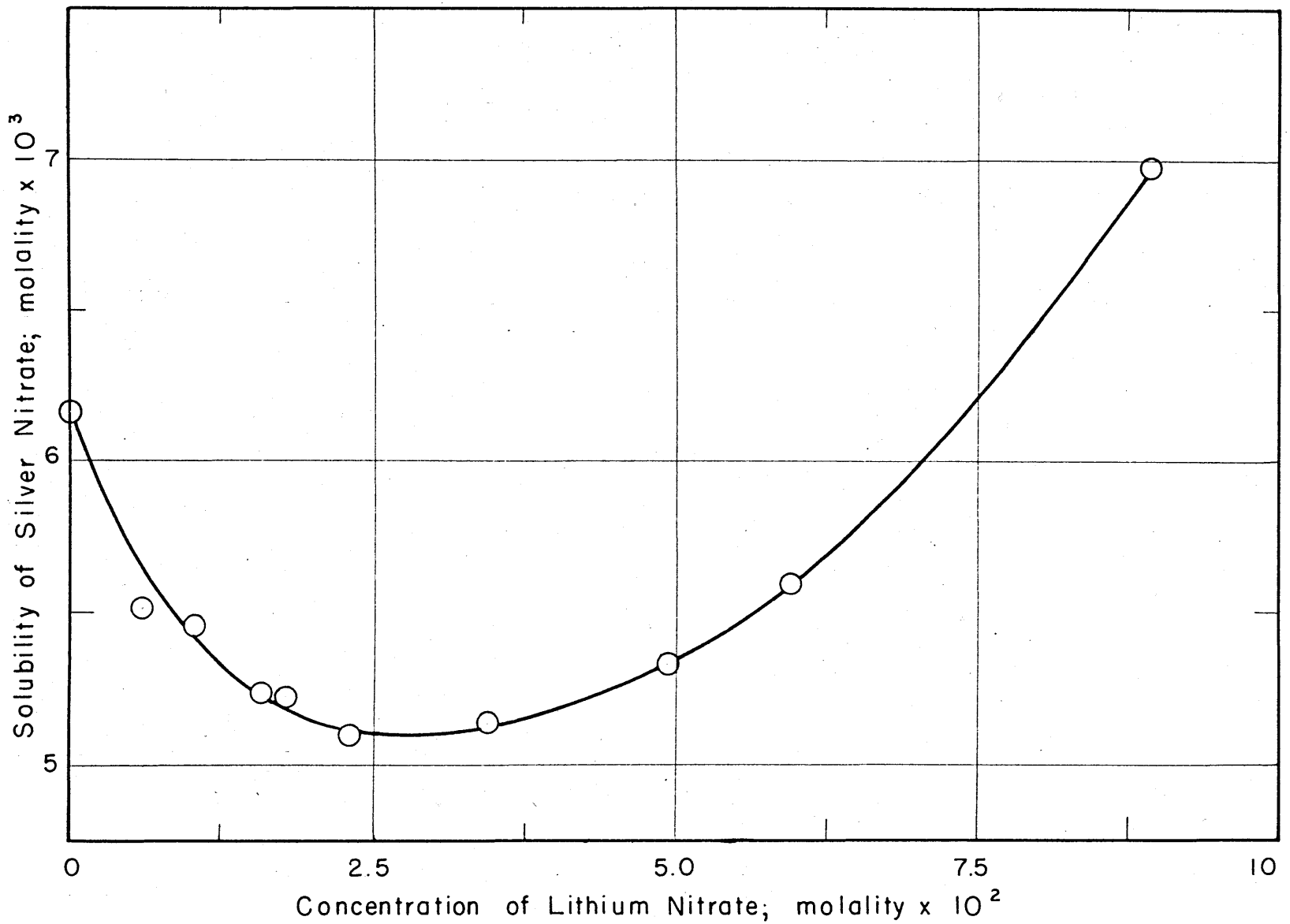

Figure VI Solubility of Silver Nitrate in the presence of Lithium Nitrate

Table VII

System Sodium Acetate- Silver Nitrate- Acetic Acid at 30°C.

Initial Concentration of Sodium Acetate C.	Solubility of Silver Nitrate S.	Solid Phase
0.0000000	0.006166	A
.0002588	.006362	A
.0007354	.006679	A
.001041	.006876	A
.003067	.008349	A
.004250	.009427	A
.006487	.009442	B
.01357	.009451	B
.02823	.009509	C
.03713	.009515	C
.03745	.009514	C
.03937	.009512	C
.04249	.009517	C
.06602	.009525	C
.06713	.009519	C
.06969	.009511	C
.09704	.009515	C

Solid phases: A, Silver nitrate; B, Silver acetate and Silver nitrate; C, Silver nitrate, Silver acetate, and Sodium nitrate

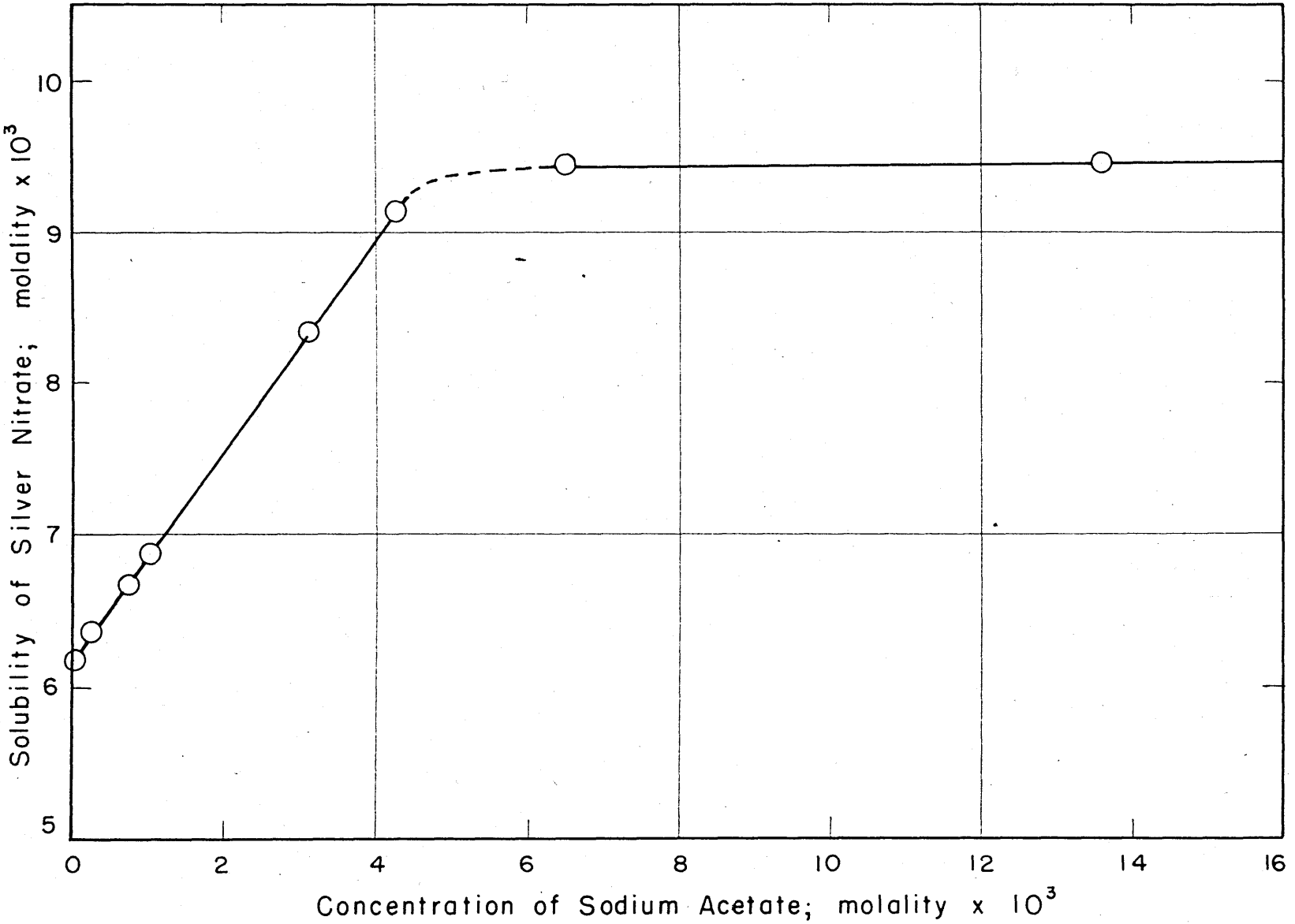

Figure VII Solubility of Silver Nitrate in the presence of Sodium Acetate

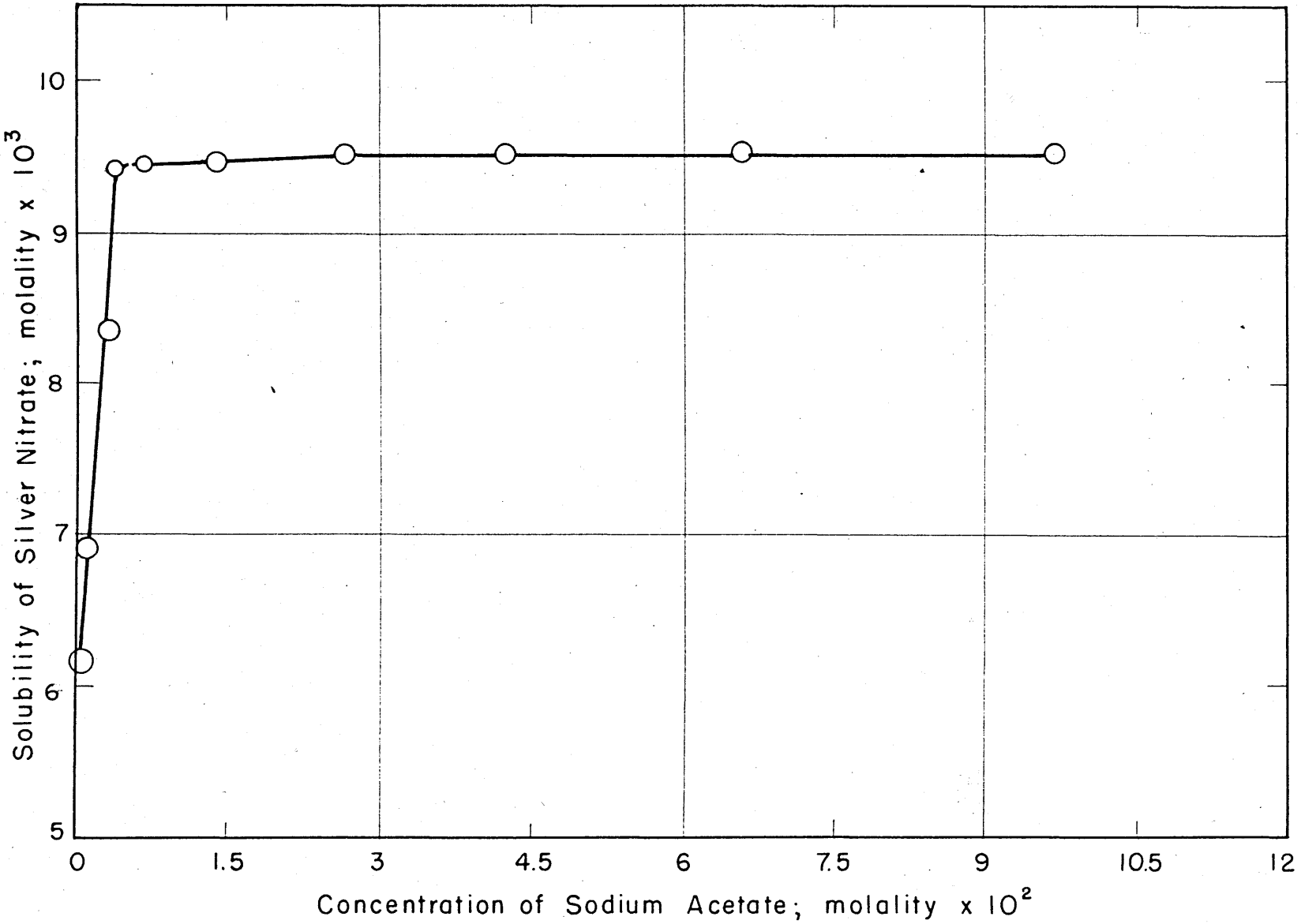

Figure VIII Solubility of Silver Nitrate in the presence of Sodium Acetate (II)

are presented in Table VI and Figure VI. The results of this study when plotted on a curve ran parallel to, but slightly lower than, the curve based upon the data of Davidson and Geer. The solubility of silver nitrate in the pure solvent was found in this investigation to be 0.006166 at 30°C. while Davidson and Geer reported at this same temperature a value of 0.00646 molal. A decrease in the solubility to approximately 0.03 molal lithium nitrate is clearly shown. Above this concentration the solubility increases.

The common-ion effect observed in these two cases may indicate a greater dissociation of the silver nitrate than appears to be usual for other salts in this solvent.

A third solvent salt, sodium acetate, was used with silver nitrate, but again the relatively low solubility of silver acetate introduced complications. In solutions with concentrations of sodium acetate ranging up to about 0.004 molal, the solubility of silver nitrate shows a sharp progressive increase, as is shown by the curve in Figure VII. In this region the solid phase is silver nitrate.

Somewhere beyond about 0.0043 molal sodium acetate the concentration of silver in solution suddenly ceases to increase rapidly, but instead shows a very gradual increase which persists until the sodium acetate concentration has reached a value lying somewhere between roughly 0.015 and 0.03 molal. In this range the appearance of the solid and its behavior with respect to settling was precisely that of a mixture of silver nitrate and silver acetate. Determina-

tion of silver in a sample of the solid obtained from one of the solutions gave a result intermediate between those calculated for silver nitrate and silver acetate. Qualitative tests showed no significant quantity of sodium in the solid.

With initial sodium acetate concentrations of approximately 0.03 molal and higher, it was found that the silver concentration in the solution became constant. From phase rule considerations this appeared to indicate the presence of three solid phases in equilibrium with the solution. A qualitative test for sodium in the solid phase showed it to be present. Two solutions of sodium acetate in acetic acid were then prepared, one 0.03564 molal and one 0.05564 molal, an excess of silver nitrate was added to each, and the mixtures tumbled for the usual period of time. A sodium analysis was run on each solution, both yielding essentially the same result, 0.02225 molal. Above this concentration of sodium acetate, therefore, the system apparently becomes isothermally invarient, in equilibrium with three solid phases, presumably silver nitrate, silver acetate, and sodium nitrate. The value of 0.02225 for the molality of sodium nitrate in solution was used in calculating the molality of silver nitrate as given in Table VII from the analytical results obtained for all the solutions above this value. The appearance of the solid, as before, resembled that of a mixture of the two silver salts. Inasmuch as Davidson and Geer (34) report the solubility of sodium nitrate in pure

acetic acid to be 0.0202 molal at 25°C., it seems reasonable to suppose that it is the third solid phase.

Taken together these results indicate the following sequence of events with progressively increased concentration of sodium acetate. At first, the solubility of silver nitrate is markedly increased, and at least one process occurring in solution would appear to be an exchange reaction producing silver acetate and sodium nitrate. At about 0.0043 molal sodium acetate the saturation value of silver acetate is reached, and silver acetate appears as a solid phase together with silver nitrate. Additional sodium acetate results chiefly in converting solid silver nitrate into silver acetate, replacing an equivalent amount of sodium acetate by sodium nitrate in solution. In this region the concentration of silver in the solution undergoes a very small increase with increase in alkali metal salt concentration. Above 0.02225 molal sodium concentration solid sodium nitrate is precipitated and the solution becomes isothermally invariant. It may be remarked that the total silver concentration in this solution is somewhat higher than in the solution phase of the isothermally invariant three-component system, Silver nitrate-silver acetate-acetic acid (See Figure X).

The systems silver acetate-uniunivalent salt-acetic acid. The effects of three different solvent salts on the solubility of silver acetate were investigated in the present work. Two of them had an ion in common with silver acetate, the

Table VIII

System Silver Nitrate-Silver Acetate-Acetic Acid at 30°C.

Concentration of Silver Nitrate C.	Solubility of Silver Acetate S.
0.0000000	0.004702
.0007541	.004606
.001957	.004257
.003421	.003832
.005208	.003371
.005939	.003174
.006790	.002966

Solid phase: Silver acetate throughout

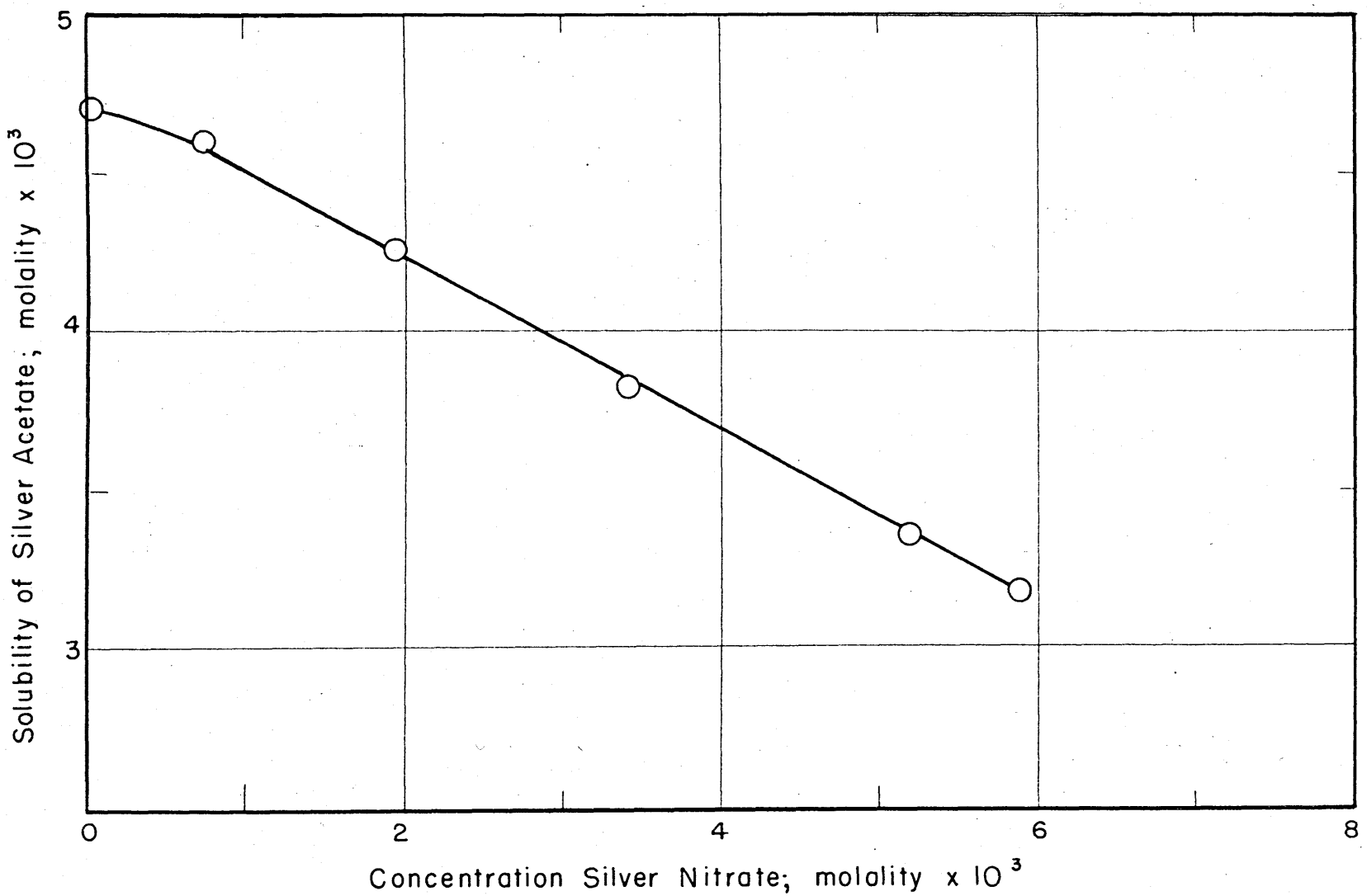

Figure IX Solubility of Silver Acetate in the presence of Silver Nitrate

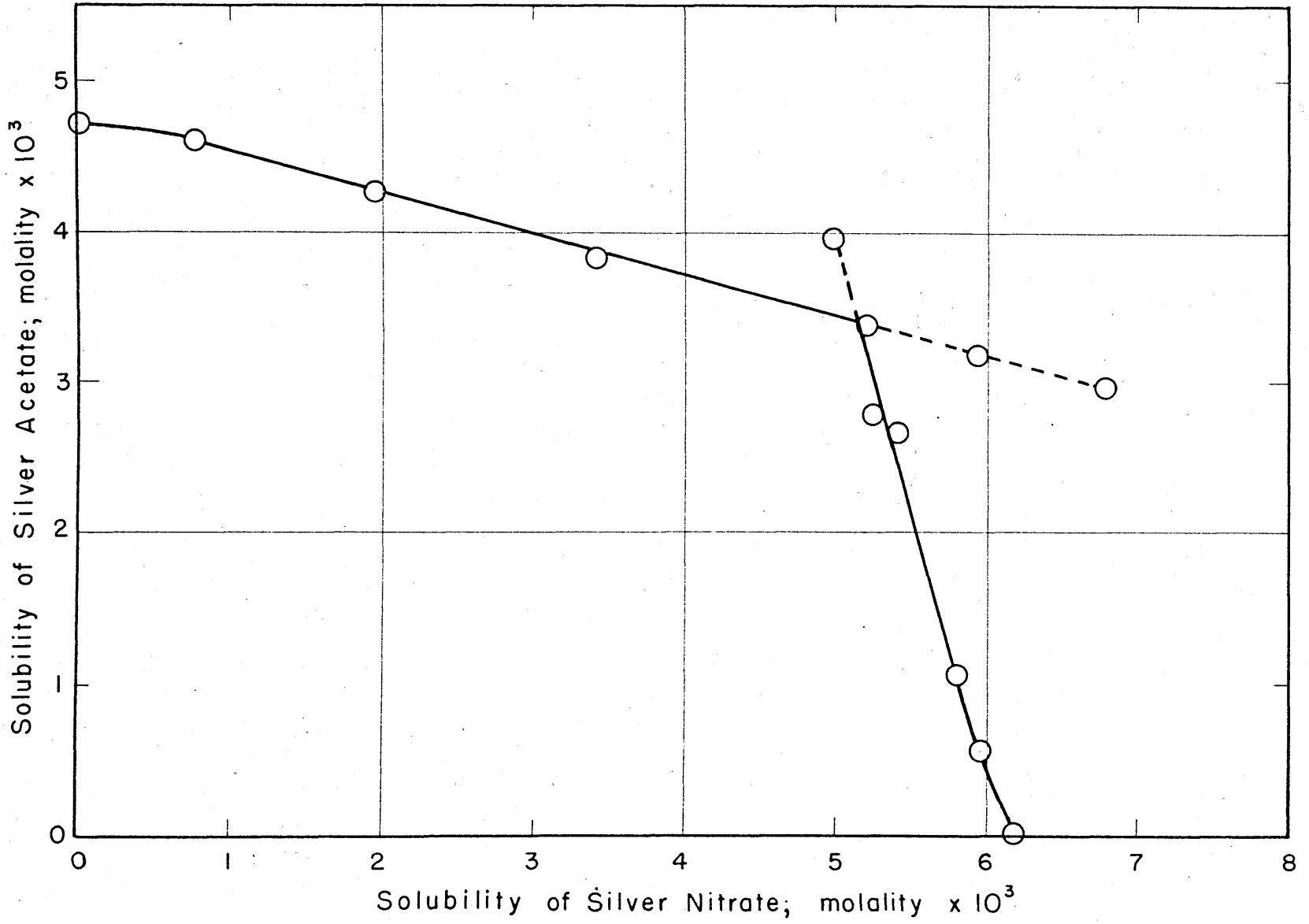

Figure X The System Silver Nitrate-Silver Acetate-Acetic Acid

Table IX

System Sodium Acetate-Silver Acetate-Acetic Acid at 30°C.

Concentration of Sodium Acetate C.	Solubility of Silver Acetate S.	K_a (equation XXIX)
0.0000000	0.004702	------
.0009294	.004722	0.0220
.002309	.004778	.0340
.002791	.004793	.0337
.01606	.005060	.0228
.02062	.005122	.0208
.02572	.005190	.0193
.02638	.005182	.0185
.03038	.005241	.0181
.03669	.005304	.0167
.03789	.005313	.0164
.04440	.005400	.0160
.05845	.005563	.0150
.07165	.005707	.0142

Solid phase: Silver acetate throughout

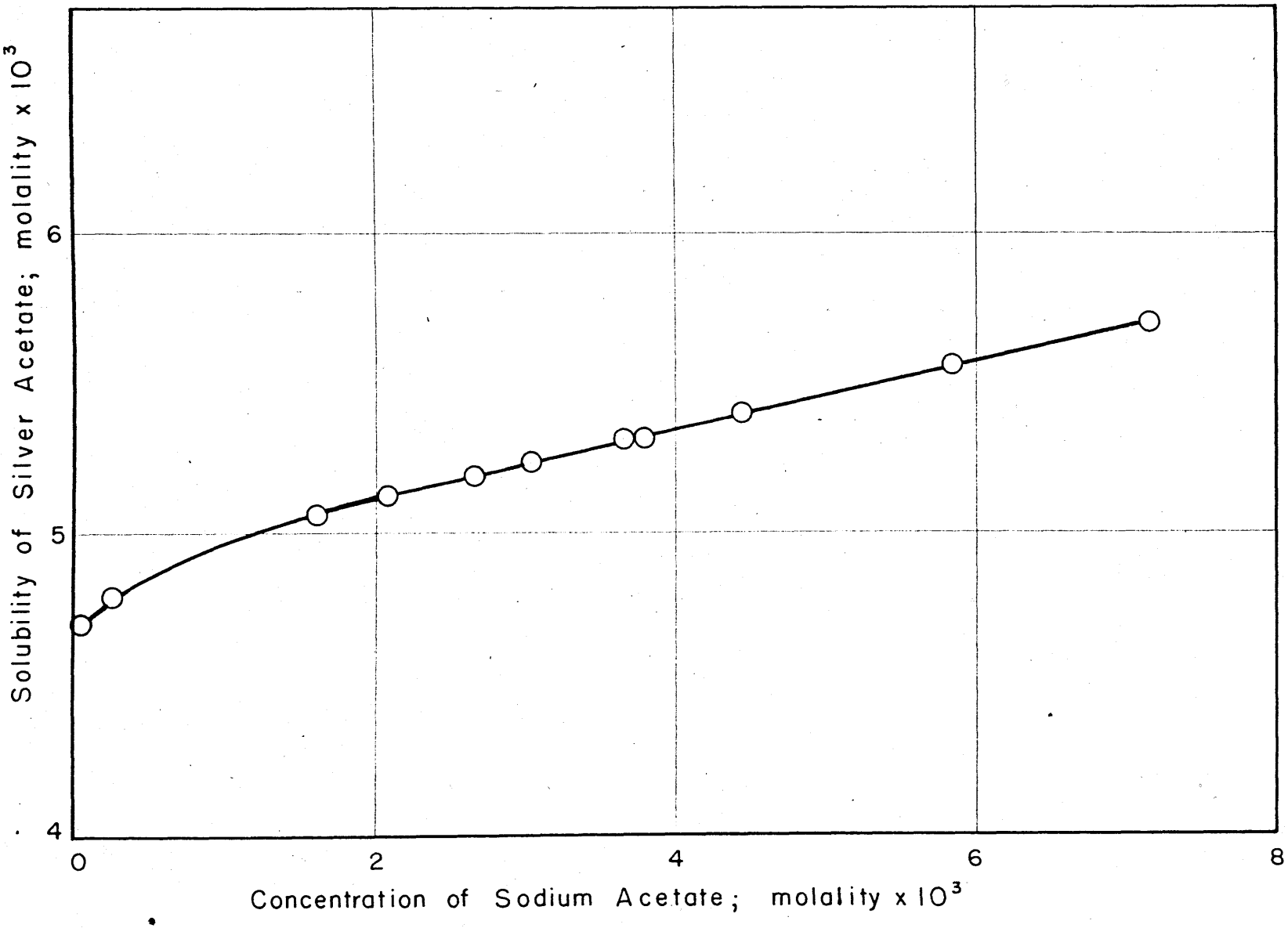

Figure XI Solubility of Silver Acetate in the presence of Sodium Acetate

Table X

System Lithium Nitrate-Silver Acetate-Acetic Acid at 30°C.

Concentration of Lithium Nitrate C.	Solubility of Silver Acetate S.	K (equation XXIX)	K (equation XXXV)
0.0000000	0.004702	---------	--------
.0004001	.004988	0.000713	0.000707
.001002	.005264	.000718	.000706
.008727	.006917	.000753	.000691
.01110	.007204	.000728	.000663
.01715	.007890	.000728	.000657
.01757	.007929	.000726	.000655
.01844	.008042	.000739	.000666
.02021	.008227	.000745	.000670
.02178	.008367	.000742	.000668
.02518	.008680	.000746	.000669
.03384	.009364	.000745	.000667
.03417	.009433	.000760	.000680
.04141	.01003	.000787	.000702
.05933	.01109	.000772	.000678
.06030	.01118	.000780	.000675
.08631	.01253	.000780	.000675
.1285	.01441	.000799	.000675
Average		.000751	.000677
Average Deviation		.000021	.000012

Solid phase: Silver acetate throughout

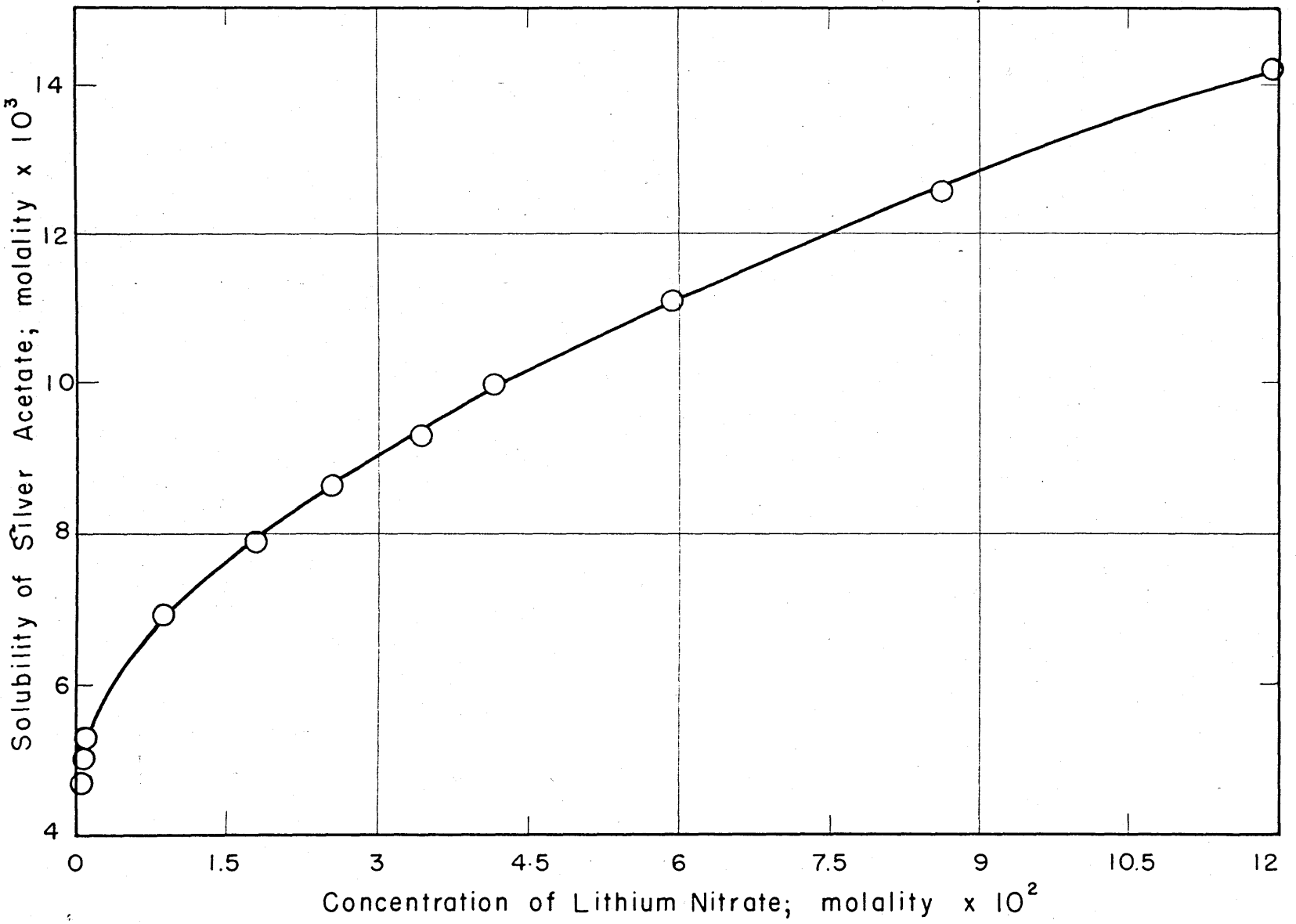

Figure XII Solubility of Silver Acetate in the presence of Lithium Nitrate

third did not. Results of the study using silver nitrate as solvent salt show that the "common-ion" effect is present (See Table VIII and Figure IX). The highest concentration of silver nitrate employed, 0.006790 molal, prepared at a temperature above 30°C., was actually somewhat above its solubility value at 30°C. which is 0.006166 molal. Nevertheless the appearance of the solid and the form of the curve shown in Figure VIII indicated that the solid phase was silver acetate alone. A gravimetric determination of silver in the solid corresponded to 99.92% silver acetate. The solubility of silver acetate in this solution was found to be 0.002966 as contrasted with 0.004702 in acetic acid alone. When the data in Tables V and VIII are plotted together, the diagram shown in Figure X results. It is seen here that both silver acetate and silver nitrate were obtained in regions of metastable equilibrium. In view of the difference in crystal structures of the two, it is perhaps not surprising that neither one appears to be very effective in inducing crystallization of the other.

The second study conducted using silver acetate as the solute salt in the presence of a salt with a common ion employed sodium acetate as the solvent salt. These results differ markedly from those described above (See Table IX and Figure XI). The difference between the two studies is immediately apparent since there is no "common-ion" effect present in the latter study. Rather, the plot of the solubility of silver acetate against the concentration of sodium

acetate (Figure XI) shows that the solubility of silver acetate initially increases rapidly, but at higher concentrations of added salt it becomes almost a linear function of the amount of solvent salt present. A weighed sample of the solid phase was titrated potentiometrically with potassium iodide solution, and it assayed at 99.92% silver acetate on the basis of the silver found. The values of the K_a, calculated by equation XXIX and tabulated in Table IX, go through a slight maximum and then decrease in a regular manner. The trend in the K_a's may be evidence that some association product is formed at the lower concentrations of added salt which is transformed into a less complex product in the more concentrated samples.

The effect of the heterionic solute salt, lithium nitrate, upon the solubility of silver acetate is to increase it at almost the rate predicted by the ion-pair exchange theory (See Table X and Figure XII). The value of the K's calculated from equation XXIV increase slowly with increasing solvent salt concentration. The average value of this K is 7.51×10^{-4} and it has an average deviation of 0.21×10^{-4}. A plot of the K_a values from Table IX against concentration of added salt, was made and from this was read the value of "K_a" corresponding to a given concentration of lithium nitrate as the added salt. This figure was then used in equation XXXV to calculate a value of K. The results of this rather arbitrary procedure gave an average K of 6.77×10^{-4} with an average deviation of 0.12×10^{-4}. The values of K

obtained in this way not only show a smaller average deviation than those from equation XXIX but also exhibit no trend. The results of this investigation give further support to the hypothesis that two processes are taking place in the acetic acid solutions. The first of these being an exchange reaction between the ion-pairs of the solute and solvent salt, and the second an association between the ion-pairs of these salts. A portion of the solid phase from the sample with a lithium nitrate concentration of 0.1285 molal was assayed at 99.92% silver acetate on the basis of the silver found and showed no evidence of the presence of silver nitrate. With initial lithium nitrate concentrations as high as this, it would be expected that solid silver nitrate, produced by metathesis, ought to appear since the total silver concentration in this instance is 0.01441 molal, considerably in excess of the highest obtained in the system silver nitrate-sodium acetate-acetic acid. It may be of course that this and perhaps some of the other solutions were actually supersaturated with respect to silver nitrate. Unfortunately seeding with some crystals of this salt was not tried.

SUMMARY

1. The solubility of ammonium bromide at 30°C. in acetic acid alone and in the presence of sodium acetate, potassium acetate, lithium acetate, and ammonium acetate of various concentrations has been determined. In pure acetic acid at this temperature ammonium bromide dissolves to the extent of 0.007692 moles per thousand grams of solvent. The three heteroionic salts all produce a marked increase in solubility, their relative effectiveness at a given concentration, decreasing in the order sodium acetate potassium acetate lithium acetate. Ammonium acetate displays no common-ion effect on ammonium bromide, but actually increases the solubility of the latter to a small extent.

2. The solvent effects of silver acetate, lithium nitrate, and sodium acetate upon silver nitrate in anhydrous acetic acid at 30°C have also been investigated. The solubility of silver nitrate in the pure solvent is 0.006166 molal. Silver acetate produces a marked decrease in solubility. Lithium nitrate also produces a pronounced initial decrease, followed by an increase at higher concentrations of solvent salt, in essential agreement with the work of Davidson and Geer (34). Sodium acetate causes a sharp increase in solubility up to a point at which silver acetate appears as solid phase. At still higher initial concentrations of sodium acetate a third solid phase, apparently sodium nitrate, appears.

3. The solubility of silver acetate in acetic acid at 30°C. has been determined to be 0.004702 molal. Its solubility in the presence of silver nitrate, sodium acetate, and lithium nitrate has also been investigated. Silver nitrate produces a decrease in solubility, but sodium acetate produces a distinct, though small, increase. Lithium nitrate produces a marked increase in solubility.

4. The validity of the hypothesis that an exchange reaction taking place between heteroionic ion-pairs may perhaps account in large measure for the neutral salt effect in anhydrous acetic acid has been examined. This hypothesis has been shown to be capable of partially explaining the salt effects found in the systems which used ammonium bromide and silver acetate as the solute salt, but in the systems using silver nitrate as the solute salt a "common ion" effect was observed. This latter phenomenon is probably due to a greater degree of dissociation of the silver nitrate ion-pair than of most of the other salts.

5. The solubility studies indicate, also, that in addition to the formation of ion-pairs some more or less complex association products are formed in at least some systems in anhydrous acetic acid.

BIBLIOGRAPHY

(1) A. L. Robinson, J. Phys. Chem. 32, 1089 (1928)

(2) R. P. Seward, and C. H. Hamblet, J. Am. Chem. Soc. 54, 554 (1932)

(3) A. W. Scholl, A. W. Hutchison, and G. C. Chandlee, J. Am. Chem. Soc. 55, 3081 (1933)

(4) C. A. Kraus and R. P. Seward, Trans. Farad. Soc. 23, 488 (1927)

(5) T. H. Gronwall, V. K. La Mer, and K. Sandved, Physik. Z. 29, 358 (1928)

(6) V. K. La Mer, T. H. Gronwall, and L. J. Greiff, J. Phys. Chem. 35, 2345 (1931)

(7) P. Debye and E. Huckel, Physik. Z. 24, 185, 305 (1923)

(8) N. Bjerrum, K. Danske Vidensk. Selsk, Mat.-fys. Medd. 1, No. 9 (1926)

(9) R. M. Fuoss, and C. A. Kraus, J. Am. Chem. Soc. 55, 476 (1933)

(10) R. M. Fuoss, Trans. Farad. Soc. 30, 967 (1934)

(11) R. M. Fuoss, Chem. Rev. 17, 227 (1935)

(12) R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. 55, 21 (1933)

(13) T. J. Webb, J. Am. Chem. Soc. 48, 2263 (1926)

(14) W. C. Eichelberger, J. Am. Chem. Soc. 56, 799 (1934)

(15) C. P. Smyth and H. E. Rogers, J. Am. Chem. Soc. 52, 1824 (1930)

(16) E. Griswold, M. Jones, and R. Birdwhistell (work soon to be published)

(17) F. M. Raoult, Ann. Chem. Phys. (6) 2, 72 (1884)

(18) F. M. Raoult and A. Recoura, Z. Physik, Chem. 5, 424 (1890)

(19) E. Beckmann, Z. Physik. Chem. 57, 136 (1907)

(20) R. P. Seward, J. Am. Chem. Soc. 56, 2610 (1934)

(21) C. A. Kraus and R. P. Seward, J. Phys. Chem. 32, 1294 (1927)

(22) L. Hansen and J. Williams, J. Am. Chem. Soc. 52, 2759 (1930)

(23) J. Williams, J. Am. Chem. Soc. 51, 1112 (1929)

(24) T. J. Webb, J. Am. Chem. Soc. 48, 2263 (1926)

(25) W. C. Eichelberger, J. Am. Chem. Soc. 56, 799 (1934)

(26) A. Noyes and W. Baxter, J. Am. Chem. Soc. 47, 2122 (1925)

(27) R. M. Fuoss, J. Am. Chem. Soc. 57, 488 (1935)

(28) A. W. Davidson, J. Am. Chem. Soc. 50, 1890 (1926)

(29) A. W. Davidson, J. Phys. Chem. 34, 1215 (1930)

(30) A. W. Davidson and W. H. McAllister, J. Am. Chem. Soc. 52, 507 (1930)

(31) A. W. Davidson, Chem. Rev. 8, 175 (1931)

(32) A. W. Davidson and E. Griswold, J. Am. Chem. Soc. 53, 1341 (1931)

(33) A. W. Davidson and V. Holn, Univ. Kansas Sci. Bul. 21, 483 (1933)

(34) A. W. Davidson and H. A. Geer, J. Am. Chem. Soc. 55, 642 (1933)

(35) A. W. Davidson and W. Chappell, J. Am. Chem. Soc. 55, 3531 (1933)

(36) A. W. Davidson and W. Chappell, J. Am. Chem. Soc. 55, 4524 (1933)

(37) A. W. Davidson and E. Griswold, J. Am. Chem. Soc. 57, 423 (1935)

(38) A. W. Davidson and H. A. Geer, J. Am. Chem. Soc. 60, 1211 (1938)

(39) A. W. Davidson and W. Chappell, J. Am. Chem. Soc. 61, 2164 (1939)

(40) E. Griswold and F. V. Olsen, J. Am. Chem. Soc. 59, 1894 (1937)

(41) E. Griswold, A. Ash, and L. MacReynolds, J. Am. Chem. Soc. 67, 372 (1945)

(42) E. Griswold and W. Van Horn, J. Am. Chem. Soc. 67, 763 (1945)

(43) A. W. Hutchison and G. C. Chandlee, J. Am. Chem. Soc. 53, 2881 (1931)

(44) I. M. Kolthoff and A. Willman, J. Am. Chem. Soc. 56, 1007 (1934)

(45) I. M. Kolthoff and A. Willman, J. Am. Chem. Soc. 56, 1014 (1934)

(46) B. V. Weidner, A. W. Hutchison, and G. C. Chandlee, J. Am. Chem. Soc. 56, 1285 (1934)

(47) B. V. Weidner, A. W. Hutchison, and G. C. Chandlee, J. Am. Chem. Soc. 60, 2877 (1938)

(48) M. M. Jones and E. Griswold, (Presented at the 123 meeting of the American Chemical Society) (1953)

(49) T. L. Smith and J. H. Elliot, (Presented at the 122 meeting of the American Chemical Society) (1952)

(50) M. M. Jones, Ph. D. Thesis, University of Kansas, (1952)

(51) J. H. Cain, Masters Thesis, University of Kansas, (1953)

(52) L. E. O. De Vissor, Rec. trav. chem. 12, 101 (1893)

(53) T. W. Richards and R. C. Wells, J. Am. Chem. Soc. 27, 459 (1905)

(54) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Organic Analysis", 3rd Edition, The Macmillan Company, New York, 1952, p. 307

(55) N. H. Furman, Editor, "Scott's Standard Methods of Analysis", 5th Edition, D. Van Nostrand, Inc., New York, 1939, Vol. I, p. 878

(56) Ibid., p. 869

(57) Ibid., p. 878

(58) C. A. Kraus and D. T. Copenhafer, J. Am. Chem. Soc. 73, 4457 (1951)

(59) C. A. Kraus and H. S. Young, J. Am. Chem. Soc. 73, 4732 (1951)